

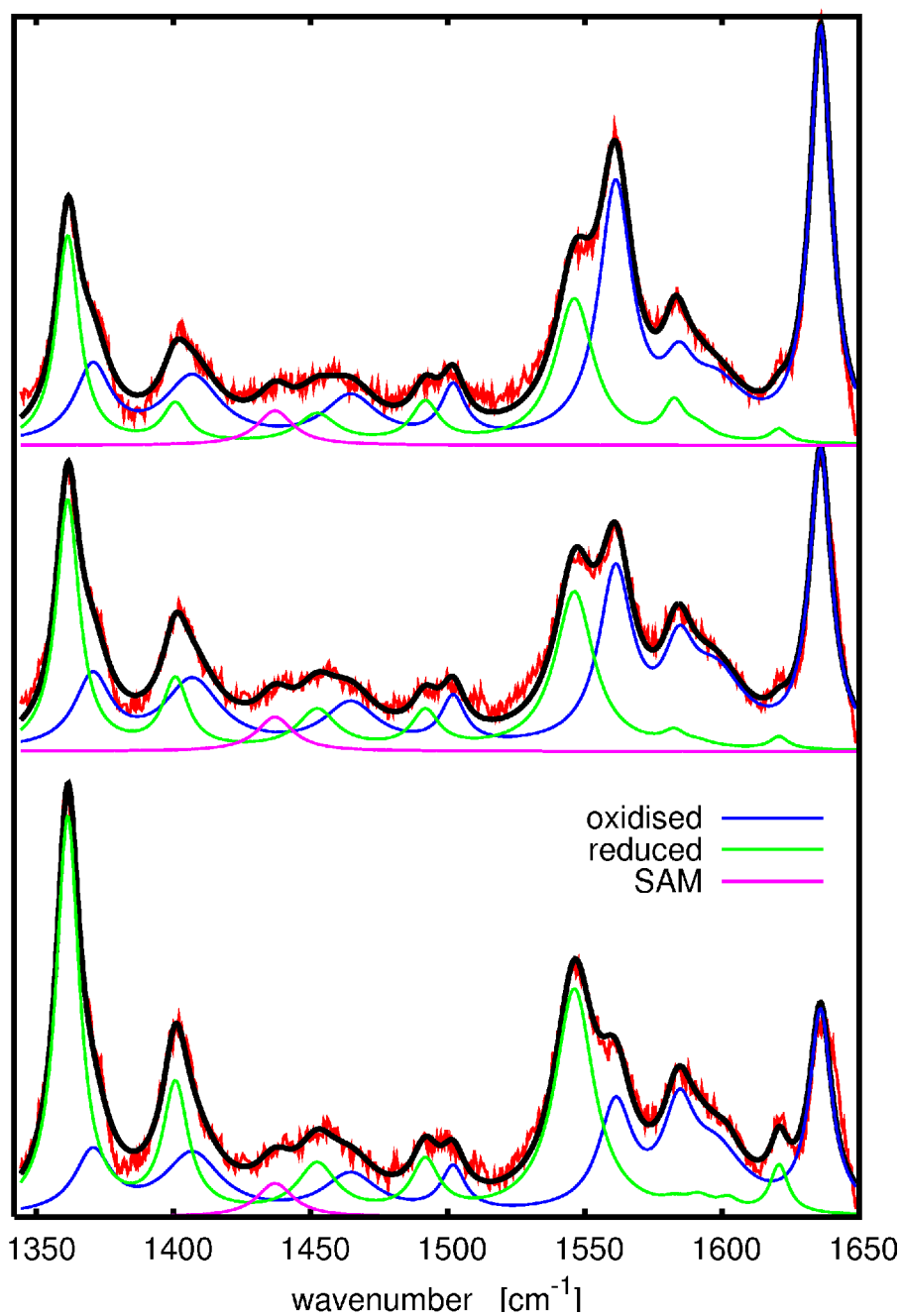
*Supporting Information for:*

**Direct Observation of the Gating Step in Protein Electron Transfer:  
Electric Field Controlled Protein Dynamics**

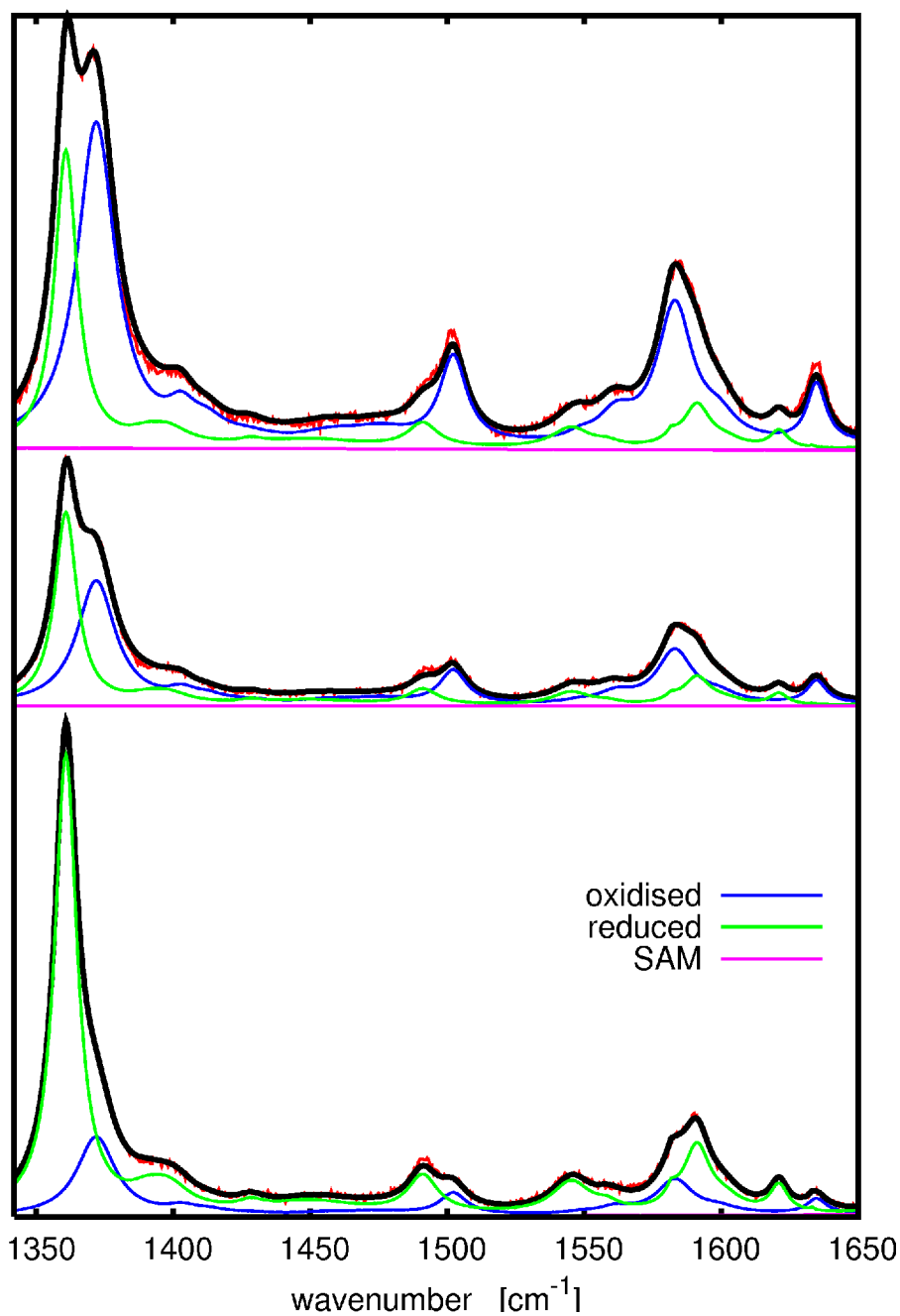
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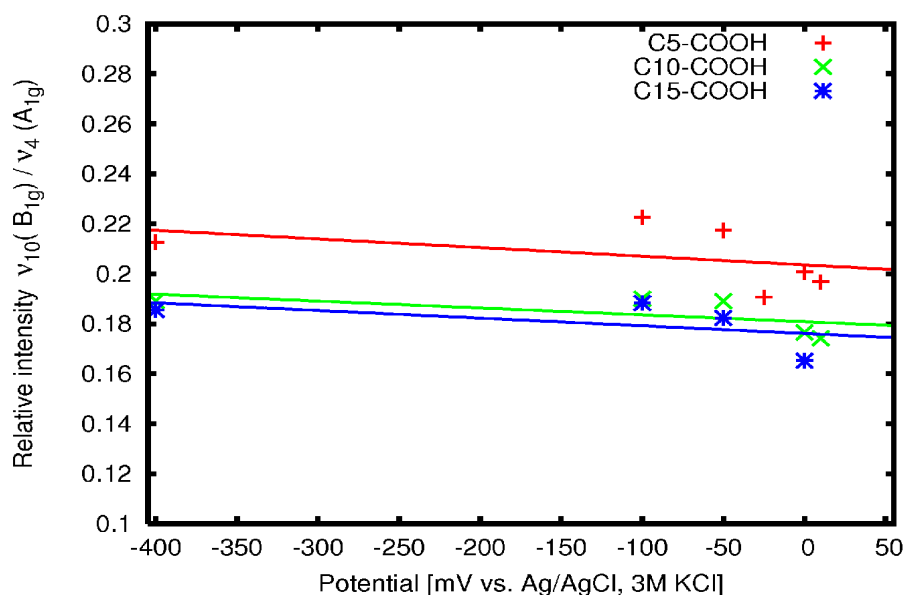
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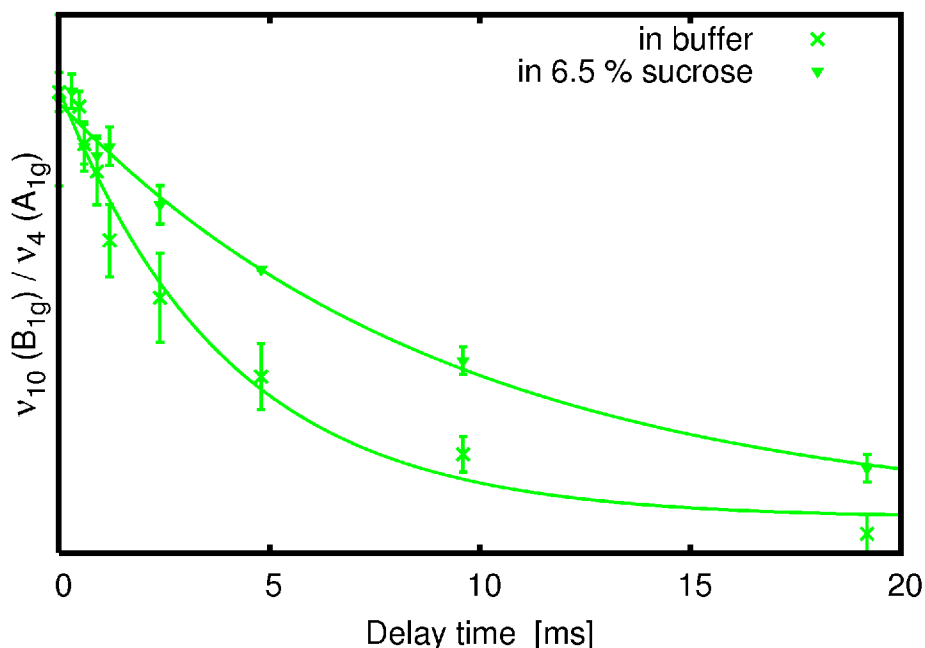
**Figure S1.** SERR spectra of Cyt electrostatically adsorbed on a  $C_5$ -coated electrode measured at different delay times (from top to bottom: 0 ms, 1.2 ms, 4.8 ms) after a potential jump from 50 to -50 mV and 514 nm excitation. Red lines: experimental spectra. Black lines: overall spectral fit. Blue lines: ferric Cyt spectral component. Green lines: ferrous Cyt spectral component.



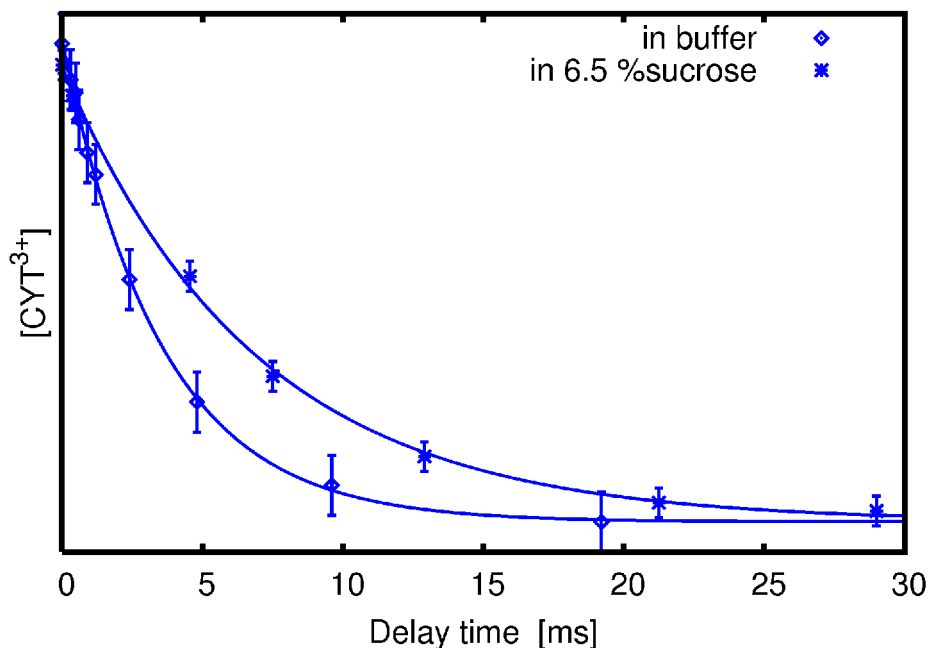
**Figure S2.** SERR spectra of Cyt electrostatically adsorbed on a C<sub>5</sub>-coated electrode measured at different delay times (from top to bottom: 0 ms, 1.3 ms, 7.6 ms) after a potential jump from 50 to -50 mV and 413 nm excitation. Red lines: experimental spectra. Black lines: overall spectral fit. Blue lines: ferric Cyt spectral component. Green lines: ferrous Cyt spectral component.



**Figure S3.** Potential dependence of the  $v_{10}(B_{1g})/v_4(A_{1g})$  intensity ratio for ferrous Cyt adsorbed on different SAMs as determined by SERR with 514 nm excitation at pH 7.0. The  $v_{10}(B_{1g})/v_4(A_{1g})$  intensity determined by RR in solution is 0.27.



**Figure S4.** Time evolution of the  $v_{10}(B_{1g})/v_4(A_{1g})$  intensity ratio for ferric Cyt adsorbed on C<sub>5</sub>-SAMs after a potential jump from 50 to -50 mV. Crosses: determination in normal buffer (12.5 mM phosphate buffer, pH = 7.0; 12.5 mM K<sub>2</sub>SO<sub>4</sub>). Triangles: normal buffer with addition of 6.5 % sucrose to increase the viscosity by ca. 20%. Measurements were performed at 514 nm excitation.



**Figure S5.** The reduction kinetics of Cyt on C<sub>5</sub>-SAMs after a potential jump from 50 to -50 mV monitored by TR-SERR at 413 nm excitation. Diamonds: determination in normal buffer (12.5 mM phosphate buffer, pH = 7.0; 12.5 mM K<sub>2</sub>SO<sub>4</sub>). Stars: normal buffer with addition of 6.5 % sucrose to increase the viscosity by ca. 20%.